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THE REMOVAL OF N-DECYL MERCAPTAN FROM HYDROCARBON
SOLVENTS BY COCONUT CHARCOAL

by

B.G. CAMERON, B.Sc.

UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA

MAY 1955

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THE UNIVERSITY OF ALBERTA

THE REMOVAL OF N-DECYL MERCAPTAN FROM HYDROCARBON
SOLVENTS BY COCONUT CHARCOAL

A DISSERTATION

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

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DEPARTMENT OF CHEMISTRY

by

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EDMONTON, ALBERTA

25 MAY, 1955

ABSTRACT

Mercaptans can be removed from petroleum products by the Doctor Process, using sodium hydroxide, or by adsorption on active carbon. An investigation of the removal of n-decyl mercaptan from benzene solution and from n-hexane solution by coconut charcoal is reported here.

The properties of mercaptans and active carbon are reviewed. The adsorption equations of Langmuir, Freundlich and Brunauer, Emmett and Teller are given as well as the method for calculation of heat of adsorption by the Clausius-Clapeyron equation.

The apparatus used in the investigation is described. A constant temperature bath and shaker were used to bring samples to equilibrium at 25°C and 35°C. Samples were prepared in a nitrogen atmosphere; special precautions were taken to exclude air. Analysis of samples was done by amperometric titration.

The disappearance of mercaptan from solution in benzene over charcoal is shown to be due to physical adsorption, oxidation by air and oxidation at the charcoal surface. The extent of this oxidation was determined by reduction of the n-decyl disulphide using amalgamated zinc and acetic acid.

More mercaptan was removed, per gram of charcoal, when hexane was used as the solvent rather than benzene. This is attributed to possible association between the benzene and the mercaptan molecules. In addition, benzene may be more strongly adsorbed than hexane. In both solvents, the amount of mercaptan removed per gram.

of charcoal decreased as the concentration of the solution was decreased. A smaller amount of mercaptan was removed from hexane solution when the temperature was raised by ten degrees.

The results of the experiments yield straight line graphs when plotted as Freundlich Isotherms but do not fit the Langmuir equation. The heat of adsorption of n-decyl mercaptan is calculated to be -1.4 k. cal. per mole.



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TABLE OF CONTENTS

	Page
Object of the Research	1
Theory	
Introduction	2
Characteristics of Mercaptans	3
Active Carbon	7
The Theory of Adsorption	10
Apparatus	17
Materials and their Preparation	23
Analysis of Samples	25
Procedure and Results	
I The nature of the removal of the mercaptan from benzene solution	28
II Oxidation of the mercaptan at the charcoal surface	31
III The effect of varying conditions on the removal of the mercaptan from solution	
(a) Concentration of the mercaptan	34
(b) Influence of the solvent	37
(c) Temperature	40
Discussion	45
Conclusions	47
Bibliography	48
List of Tables	i
List of Figures	ii
List of Plates	iii

LIST OF TABLES

	Page
Table IA	Concentrations of benzene solutions. 30
Table IB	Grams of n-decyl mercaptan removed from benzene solution per gram of coconut charcoal at 25°C. 30
Table II	Grams of n-decyl mercaptan removed from 0.1982 M benzene solution per gram of coconut charcoal at 25°C. 33
Table IIA	Grams of n-decyl mercaptan removed from 0.1026 M benzene solution at 25°C. 33
Table III	Removal of n-decyl mercaptan from benzene solution at 25°C.
Table IV	Removal of n-decyl mercaptan from hexane solution at 25°C. 39
Table V	Removal of n-decyl mercaptan from hexane solution at 35°C. 40

LIST OF FIGURES

		Page
Figure 1	Removal of n-decyl mercaptan from benzene solution by coconut charcoal at 25°C. (Composite graph.)	32
Figure 2	Removal of 0.1982 M n-decyl mercaptan from benzene solution by coconut charcoal at 25°C.	35
Figure 2A	Removal of 0.1026 M n-decyl mercaptan from benzene solution by coconut charcoal at 25°C.	36
Figure 3	Removal of n-decyl mercaptan from benzene solution by coconut charcoal at 25°C. Freundlich Isotherm.	38
Figure 4	Removal of n-decyl mercaptan from hexane solution by coconut charcoal at 25°C. Freundlich Isotherm.	41
Figure 5	Removal of n-decyl mercaptan from hexane solution by coconut charcoal at 25°C. and 35°C. Freundlich Isotherms.	43
Figure 6	Removal of n-decyl mercaptan from hexane solution by coconut charcoal at 25°C. and 35°C. Langmuir Isotherms.	44

LIST OF PLATES

	PAGE
Plate 1 The Constant Temperature Bath	19
Plate 2 The Nitrogen Apparatus and Furnace	20
Plate 3 The Amperometric Titration Apparatus	22

Object of the Research

The purpose of this work has been to investigate the removal of mercaptans from hydrocarbon solvents by coconut charcoal. Benzene and n-hexane were chosen as solvents and n-decyl mercaptan was used because of its relatively inoffensive odor and low susceptibility to oxidation. The adsorptive property of charcoal has been used in the removal of mercaptans during the refining of crude oils and in the processing of petroleum products for market.

The investigation of this problem has been divided into three phases, viz:

I) The nature of the removal of the mercaptan from benzene solution.

II) Determination of the amount of oxidation of the mercaptan at the charcoal surface.

III) The effect of varying conditions on the removal of the mercaptan from solution:

(a) Concentration of mercaptan.

(b) Influence of solvent.

(c) Temperature.

Previous study (18) had already indicated that removal of the mercaptan from benzene solution showed the characteristics of adsorption. However it was evident that some oxidation of the mercaptan was occurring.

THEORY

Introduction

Mercaptans were discovered in 1834 by the Danish chemist Zeise (20). The sulphur compounds, while objectionable as to odor, are becoming more prominent as a wider variety of uses are found for them. Gasoline which contains mercaptans is corrosive, has a low octane rating and possesses a disagreeable odor. For these reasons it is important that mercaptans be removed during the refining of crude oils.

The Doctor process (9) for the elimination of mercaptans consists of treatment of "sour" gasoline with lead oxide and aqueous sodium hydroxide; the resulting sodium plumbite reacts with mercaptans to produce lead mercaptides:

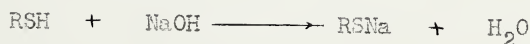


Subsequent addition of sulphur results in the formation of disulphides while the black lead sulphide is precipitated:



Gasoline is said to be "Doctor Sweet" when the addition of sulphur produces no precipitate of lead sulphide. Disulphides remain after this process however.

The octane rating of gasoline is improved if sulphur compounds are completely removed. This is accomplished by treatment with sodium hydroxide:



This treatment works well with mercaptans of small carbon chains. Higher mercaptans do not occur to a great extent in gasoline.

Characteristics of Mercaptans

A. General

Mercaptans are thioalcohols i.e., alcohols in which the oxygen of the alcoholic group is replaced by sulphur (2). They are more acidic than alcohols and only slightly associated. Mercaptans have characteristic odors ranging from the nauseating smell of methyl mercaptan to relatively pleasant odors of the higher members. They are slightly yellow or colorless liquids. Myricyl mercaptan ($C_{16}H_{33}SH$) is a solid.

B. Physical Properties.

Physical properties of mercaptans from methyl to nonyl have been determined by Ellis and Reid (7). As the series is ascended, melting points, boiling points and densities increase as do these properties for corresponding alcohols. In the lower members of the series, melting and boiling points are lower and densities are higher for mercaptans than for alcohols. These properties become similar as the higher members are reached. The latent heat of vaporization for some mercaptans has been calculated by the same authors. There is an increase from - 8,847 calories per mole for amyl mercaptan to - 11,522 calories per mole for nonyl mercaptan.

Physical properties for n-decyl mercaptan have been determined by Noller and Gordon (28).

These are:

B.P. 125-7°C (19mm)

d_{20}^{20} 0.8410

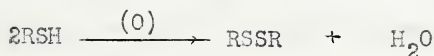
n_D^{20} 1.43367

C. Chemical Properties

Like alcohols, the mercaptans undergo esterification and they react with aldehydes to give mercaptals. Mercaptans display superior activity to alcohols in their reaction with ketones:



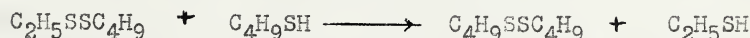
Mild oxidation of alcohols produces aldehydes. Similar treatment of mercaptans forms disulphides:



The effect of oxidation of mercaptans by the atmosphere has been investigated (31) and has been shown to occur quite readily in the presence of alkalis. Oxidation decreases as the mercaptan series is ascended. Mercaptans are also oxidized by concentrated sulphuric acid, nitric acid, potassium permanganate, hypochlorites and halides. Iodimetric determination of mercaptans is possible from the quantitative reaction:



Reduction of disulphides is accomplished with zinc and acetic acid (11) or by another mercaptan:



Use is made of this property in the permanent waving of hair. Application of mercaptan to the hair breaks down the cross links due to cystine units in the protein chain by reducing cystine to cysteine. Exposure to air reforms the cross links to give the new set.

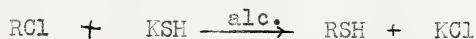
Thioethers are formed by sodium mercaptides and alkyl halides after the fashion of the Williamson synthesis:



The reaction occurs rapidly at room temperature.

Mercaptides of heavy metals are formed instantly upon addition of mercaptan to solutions of the metal ions. The light yellow salts are more stable in organic solution. The affinity of thioalcohols for heavy metal oxides gave rise to the name mercaptan (corpus mercurio aptum) (2). Use is made of this characteristic in petroleum refining as set out above and in the amperometric titration of mercaptans with silver nitrate (21).

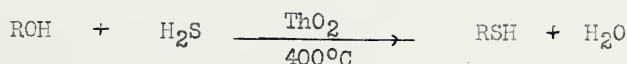
The various mercaptans can be prepared (14) from alkyl halides and potassium or sodium hydrogen sulphide:



in which the following side reaction occurs:



or from alcohol and hydrogen sulphide using thorium oxide as a catalyst:



D. Uses

A variety of uses are found for mercaptans and mercapto der-

ivatives. Among these the following may be listed: (9, 10)

- 1) Ethyl mercaptan is used together with acetone in the manufacture of the hypnotic, sulphonal.
- 2) Mercaptans are used to control emulsion polymerization of rubber and as masticators in the impregnation of leather with rubber. The vulcanization of rubber is accelerated by 2-mercaptobenzothiazole.
- 3) Permanent waving.
- 4) Corrosion inhibitors in oil well brines.
- 5) The lower mercaptan members are used as odorants for natural gas.

Active Carbon

A. General

A material which may be used to remove mercaptans from organic solvents is active carbon. The ability of charcoal to remove coloring matter and impurities from solutions and to adsorb gas has been recognized for many years. The earliest experimental use of wood charcoal is attributed to C.W. Scheele in 1773. An experiment showing the removal of a gas by charcoal was conducted by Abbe F. Fontana in 1777. The purification of water by charred wood was noted by Lowitz (Russia) in 1785 and the use of charcoal to purify wines was reported by E.O. von Lippman as early as 1788. A water purification system was constructed for the sewers of the city of London, England in 1866, use being made of charcoal filters. The rapid development of the sugar industry in Europe in the nineteenth century was due to the use of wood charcoal for the clarification of sugar liquors. (3)

Early charcoals were prepared by burning wood of various kinds; later, blood and bone charcoals were prepared. The use of coconut and nut shells as starting materials became prominent during the first World War. Coconut charcoal was used for respirators because of its high adsorptive properties. Up to 1942 a total of 110 carbon adsorbents were commercially prepared in the United States and Europe.

B. Preparation

The preparation of active carbon is based upon increasing the surface area of a charcoal by burning off hydrocarbon impurities leaving only the basic carbon structure of the original

material. Two methods (8) are in use, viz;

1) Chemical

The raw material is carbonized at 600°C in the absence of air and then ignited at elevated temperatures to remove volatile materials. Elements other than carbon are then added to increase the activity of the charcoal. ZnCl_2 has been found to be the most effective in this way. In a typical process, several parts of zinc chloride are added to one part of the carbonaceous material which is then ignited in a rotary kiln.

2) High Temperatures

After ignition, the charcoal is treated with a carbon dioxide stream or with air at temperatures ranging from 800°C to 900°C to remove residual hydrocarbons and to erode the charcoal surface. Since this process involves loss of carbon, there is a limit to the time of treatment.

Coconut charcoal is treated by mixing Dolomite (CaMgCO_3) with the husks before ignition. Activation is completed by oxidation with carbon dioxide.

Surface areas of $2-6 \times 10^4 \text{ cm}^2$ per gram are claimed for active carbons. Adsorption is attributed to capillaries, surface area and active centres of the carbon structure (15, 16, 17).

C. Uses

The following specific applications are found for active carbons:

a. Sugar refining---removal of impurities from sugar liquors.

- b. Removal of soaps and peroxides from edible oils.
- c. Improvement of color and flavor of other foodstuffs.
- d. Removal of impurities from chemicals and pharmaceuticals.
- e. Removal of disagreeable odors from whiskey.
- f. Reclaiming of solvents.
- g. Removal of chlorine from water supplies following chlorination.
- h. Catalysis, e.g. in the production of sulphonal.
- i. Respirators and gas masks.

Theory of Adsorption

A. General

The phenomenon of taking up gases by liquid and solid surfaces was termed absorption by early workers (3). The term "sorption" was proposed by McBain (27) to account for the rapid initial uptake of gases by solid adsorbents and the slower process of diffusion which follows. The term "adsorption" attained prominence in the latter part of the nineteenth century.

Adsorption has received attention from many workers and various theories have been advanced to account for the retention of molecules on liquid and solid surfaces. Some of these theories will be considered.

B. The Langmuir Equation

As a result of his study of the fundamental properties of solids, Langmuir (24, 25) developed an equation for the adsorption of gases by solids. According to this writer, the forces acting on molecules at a solid surface are purely chemical. Molecules are retained by primary or secondary valence and in many cases the stronger primary binding apparently occurs.

Langmuir has stated that the cause of adsorption is a time lag between the arrival of a molecule at the surface and its return to the gaseous phase. It is assumed that a molecule striking the bare surface does not immediately leave and furthermore that a molecule which strikes another already adsorbed returns immediately to the gaseous phase. This leads directly to the conception of a monomolecular adsorption layer. In addition, the heat of adsorption

of each molecule is assumed to be the same.

Let the fraction of a surface which is bare be represented by Θ and that fraction which is covered by adsorbed molecules be Θ_1 . At a state of equilibrium the number of molecules arriving at the surface will be equal to the number of molecules departing to the gaseous phase. The rate of condensation of the molecules will be proportional to the number of molecules striking each square centimeter of the bare surface; similarly the number of molecules evaporating from the surface will be proportional to the number of molecules adsorbed; hence

$$\alpha \Theta \mu = v_1 \Theta_1 \quad (1)$$

where α is a constant usually less than unity.

μ is the number of molecules striking each square centimeter of the bare surface.

v_1 is the rate at which molecules would evaporate if the surface were entirely covered and is therefore a constant for constant temperature.

since

$$\Theta + \Theta_1 = 1 \quad (2)$$

therefore

$$\Theta_1 = \frac{\alpha \mu}{v_1 + \alpha \mu} \quad (3)$$

which is Langmuir's adsorption equation.

For low temperatures and therefore low values of v_1 the amount of adsorption should be larger and nearly independent of the gas pressure. At higher temperatures, the amount of adsorption would

be small and proportional to pressure. At low pressures the amount of gas adsorbed is small and proportional to the gas pressure. The surface becomes slowly saturated at high pressures.

To test the applicability of this equation to experimental data, the following procedure may be taken. The pressure of a gas and the concentration of a solution are analogous and both are proportional to the number of molecules striking a surface. The amount of substance adsorbed is proportional to the surface covered. Let X represent the amount of a substance adsorbed from solution and C the concentration of the solution, then:

$$x = k_1 \theta, \quad (4)$$

$$c = k_2 \mu \quad (5)$$

where k_1 and k_2 are proportionality constants.

From equation (3):

$$x = \frac{\alpha \mu k_1}{v_1 + \alpha \mu} = \frac{\alpha k_1 c / k_2}{v_1 + \frac{\alpha}{k_2} c}$$

$$x = \frac{k_1 \alpha}{k_2 v_1} \left(\frac{c}{1 + \frac{\alpha}{v_1 k_2} c} \right) \quad (6)$$

Combining constants and rearranging.

$$\frac{c}{x} = \frac{1}{R'} + \frac{R''}{R'} c \quad (7)$$

Therefore a plot of $\frac{c}{x}$ versus c should yield a straight line having a slope equal to $\frac{R''}{R'}$ and ordinal intercept equal to $\frac{1}{R'}$, if the conditions of adsorption are as set down in the derivation.

C. The Freundlich Equation

To account for his observations of Adsorption from dilute solutions by adsorbents such as meerschaum, talc, coconut charcoal, blood charcoal and sulphur, Freundlich (12) has proposed an equation of the form:

$$\frac{x}{m} = k p^{\frac{1}{n}}$$

in which x is the amount of a substance adsorbed.

m is the weight of adsorbent.

p is the concentration of the adsorbate.

and k & n are constants dependent on the temperature and the nature of the adsorbent.

Taking logarithms:

$$\log_{10} x/m = \log_{10} k + 1/n \log_{10} p$$

thus a plot of $\log_{10} x/m$ vs. $\log_{10} p$ should yield a straight line of slope $1/n$ and ordinal intercept $\log_{10} k$. Freundlich points out that a better value for k is obtained if it is calculated for several concentrations and the mean is taken rather than obtaining k by extrapolation. This is because of slight bends which he found in his plots.

Freundlich arrived at his equation empirically by observing that in all his experiments with dilute solutions a parabolic curve was obtained by plotting the amount of a substance adsorbed versus its initial concentration.

He approached the problem of adsorption by considering surface tension of solutions. The greater the surface tension of a liquid, the greater is the amount of work required to bring a mole of the substance to the body from the surface layer of the liquid. Thus for solutions of high surface tension less adsorption should be observed. By Traub's Rule, the surface tension of members of a homologous series increases with increasing molecular weight; thus adsorption should become less for the higher members of a series. Freundlich reports apparent reversal of this rule and accounts for it by the orientation of the saturated groups toward the surface. The same phenomena has been reported by Holmes and McKelvey (19).

In discussing the effect of solvent upon the extent of adsorption, Freundlich points out that if the solvent is strongly adsorbed, the solute will be weakly adsorbed and vice versa.

D. Multimolecular Adsorption

It is possible that molecules, when striking other already adsorbed, do not immediately return to the gaseous phase but are retained to form other layers on top of the first. This could occur if the forces of attraction between the adsorbed and impinging molecules were sufficiently great. Brunauer, Emmett and Teller (4) have derived an equation to account for such behavior in adsorption. The equation takes the form:

$$v = \frac{K p v_m}{(q^0 - p) [1 + (K-1) p/q]}$$

where v is the volume of gas adsorbed.

v_m is the volume of gas adsorbed when the surface is covered by a complete monomolecular layer.

p is the gas pressure.

k and q_0 are constants.

When only one layer of molecules is adsorbed, this equation reduces to:

$$\frac{p}{V} = \frac{p_0}{C v_m} + \frac{p}{v_m}$$

where p_0 is the saturation pressure of the gas.

C is a constant derived from the heat of liquifaction of the gas.

The last equation is clearly a special form of the Langmuir equation.

E. The Heat of Adsorption

Measurements of heats of adsorption have been undertaken by several workers over a considerable period of time. Particular attention has been paid to the heat evolved upon the adsorption of gases by solids and several ingenious types of apparatus have been designed for this purpose. Beebe and Orfield (1) have measured the heats of adsorption of hydrogen on chromic oxide and carbon monoxide on copper at -163°C . These workers made use of thermocouples in their experiments. An ice calorimeter has been used by Marshall and Bramston-Cook (26) to measure the heat of adsorption of oxygen on charcoal and by Lamb and Ohl (23) for a number of gases.

The heat of adsorption from solution may be calculated by means

of the Clausius-Clapeyron equation (5) (30) in the form:

$$\Delta H_{ads} = \frac{RT_1 T_2}{(T_2 - T_1)} \ln \frac{C_2}{C_1}$$

where ΔH_{ads} is the heat of adsorption in calories per mole.

R is the gas constant in calories per mole per degree.

T_1, T_2 are absolute temperatures at which

C_1, C_2 are concentrations in equilibrium with fixed values
of x/m .

It has been pointed out by Ganguli (13) that the heats of adsorption for such gases as argon, nitrogen, carbon monoxide and several others are very nearly equal to their heats of sublimation. This author concludes that the process of adsorption is essentially one of condensation.

It has been found (6) that the heats of adsorption of gases on graphite are not constant over the whole adsorption time but decrease to about one half the initial value with increasing adsorption. This phenomenon is attributed to active centers on the surface of adsorbents. The initial adsorption occurs at these centers and the heat of adsorption falls off after they are saturated. Such active centers are held by Hassler and McMinn (17) to be responsible for the specific adsorption of some substances by various adsorbents.

APPARATUS

1) The Constant Temperature Bath

The detail of this apparatus is shown in Plate 1.

Temperatures were maintained in the bath by means of two heaters (D,E) which were controlled by a mercury thermoregulator (F) and a relay (A). A 125 watt heater was used continually at both 25.0°C and 35.0°C. For the lower temperature a 125 watt intermittent heater was used; this was changed to a 250 watt heater for the higher temperature. Temperatures were held within $\pm 0.1^\circ\text{C}$ by this arrangement. The temperatures were read by means of a 0.1°C thermometer inserted into the bath between the thermoregulator and the intermittent heater. No visible variation in temperature was noted. The distilled water of the bath was kept in motion by means of a centrally located stirrer (B).

The shaking apparatus (C) consisted of a motor having a cone driven shaft to which was attached a brass strip bent at right angles and attached to a notched plywood board running the length of the bath. The 4 oz. bottles were held in place in the notches by means of stopper ties attached to flat head screws set in the board. A shaking rate of 150 times per minute was maintained.

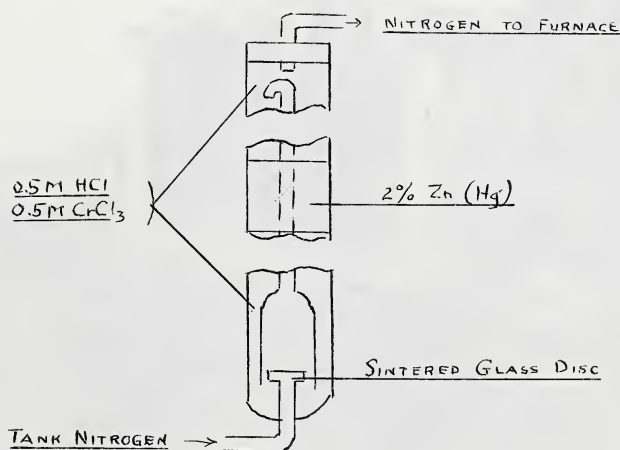
To keep the water of the bath free of suspended particles and dust, a 400 ml. beaker was placed on the bottom and to one side. This acted as a trap and kept the bath water quite clear.

2) The Nitrogen Purifier and Furnace

The detail of this apparatus is shown in Plate 2.

Oxygen was removed from tank nitrogen by passing the gases through

a $\text{CrCl}_2\text{-Zn(Hg)}$ column (A-B). The solution for the column was 0.5 M CrCl_3 in 0.5M HCl . The gases entered the column at the bottom through a sintered glass disc and passed upward through CrCl_2 in a glass tube. The oxidized solution, carried upward by the gas, was reduced on passing through the Zn(Hg) layer on its way to the bottom of the column. The Zn(Hg) layer consisted of 200 gm. of amalgamated 20-30 mesh zinc metal. Glass beads were mixed with the metal to prevent plugging of the column. This arrangement is shown schematically below:



On leaving the column the nitrogen passed through saturated HgCl_2 , concentrated NaOH and concentrated H_2SO_4 (C) to remove CrCl_3 , HCl and H_2O . The gas was divided at D; one stream was led to the surface of a charcoal sample in the furnace (E), the other to a hypodermic needle at the end of a length of rubber tubing. The latter stream was used to provide a nitrogen atmosphere over the charcoal samples at the completion of evacuation and to maintain a nitrogen atmosphere at the time of withdrawal of aliquots for titration. A mercury column was provided between the nitrogen tank and the $\text{CrCl}_2\text{-Zn(Hg)}$ column to avoid possible damage due to too great gas pressure.

THE CONSTANT TEMPERATURE BATH



Plate 1.

- A. Relay
- B. Stirrer
- C. Shaker motor.
- D.-E. Heaters.
- F. Thermoregulator.

THE NITROGEN APPARATUS AND FURNACE

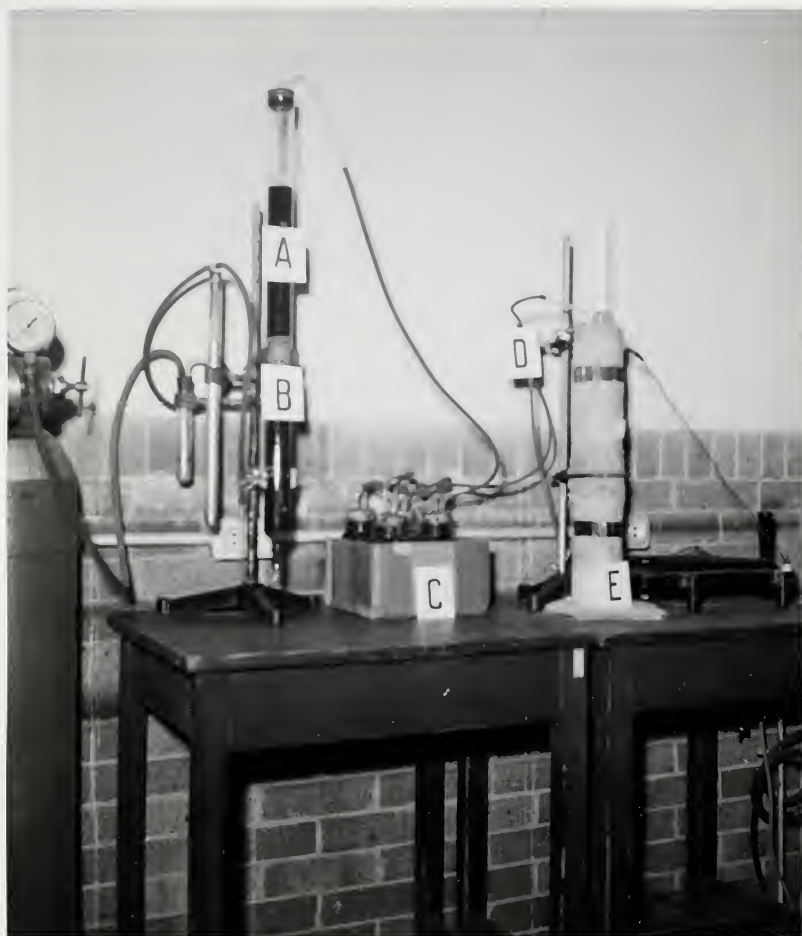


Plate 2.

- A.-B. $\text{CrCl}_2\text{-Zn(Hg)}$ column
C. $\text{HgCl}_2\text{-NaOH-H}_2\text{SO}_4$
D. N_2 leads to furnace and bottles.
E. Furnace.

The furnace, used to heat the charcoal samples to $300^{\circ}\text{C} \pm 3^{\circ}\text{C}$ was constructed by wrapping nichrome wire, having a resistance of 0.654 ohms per foot, around an asbestos covered length of stove pipe 3 inches in diameter. A second layer of asbestos covered this wire. A tripod (not shown in Plate 2) was constructed to hold to 4 oz. bottles approximately in the middle of the furnace. Nitrogen was led into the bottles in the furnace by means of a Pyrex glass tube. Temperatures were controlled by a resistance in the circuit and were read by means of a 360°C thermometer held centrally in the furnace opening.

3) The Amperometric Titration Apparatus

The detail of this apparatus is shown in Plate 3.

The apparatus was constructed according to the specifications of Kolthoff and Harris (21) and consisted of an Hg-HgI_2 half cell, a microammeter, a 10 ml. microburette and a rotating platinum electrode.

The half cell (A) was made up by placing a solution of 4.2 g. KI and 1.3 gms. HgI_2 in 100 mls. saturated KCl over a layer of Hg in a 125 ml. sidearm erlenmeyer flask. The cell was connected by means of plastic tubing to a salt bridge in a sintered glass tube (B). The salt bridge consisted of 30% KNO_3 in 3% agar. The KNO_3 helped to prevent the passage of chloride ions from the cell into the titration solution. As a further precaution against chloride ions, another sintered glass tube containing saturated KNO_3 solution was placed over the salt bridge. An 18 mm test tube containing distilled water provided a convenient cover for the sintered glass tubes.

THE AMPEROMETRIC TITRATION APPARATUS

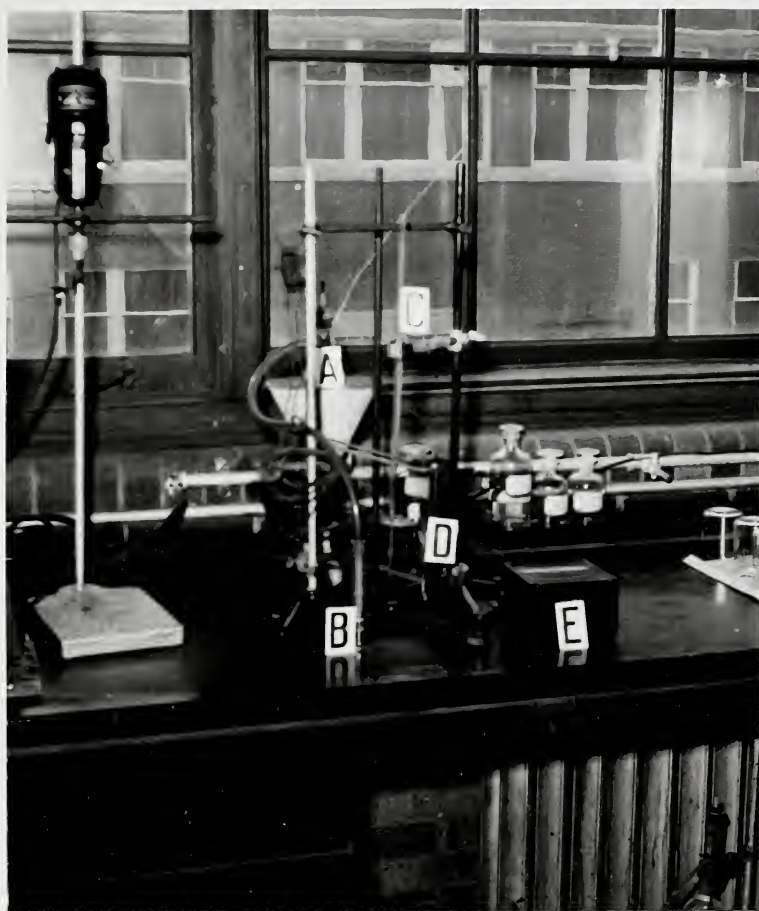


Plate 3.

- A. Hg-HgI₂ Cell.
- B. Salt bridge (3% agar-30% KNO₃)
- C. 10 ml. microburette.
- D. Rotating platinum electrode.
- E. Microammeter.

The rotating platinum electrode (D) was made by sealing a one inch piece of platinum wire in the end of a soft glass tube which was then bent away from the direction of spin thus:



The tube was then filled with mercury. The electrode was rotated approximately 450 time per minute by a small constant speed motor.

The circuit was completed by connecting the half cell and the rotating electrode to a microammeter (E) using fine copper wire.

Air bubbles in the plastic tubing from the cell were minimized by placing the cell well above the bench. A thin layer of grease at the top of the flask prevented creeping by the salts of the cell. The microburette was conveniently held in a cutaway cork by a burette clamp and could be swung over the titration flask as required.

MATERIALS AND THEIR PREPARATION

The following materials were used:

- (a) 6-12 mesh coconut charcoal, supplied by the City Chemical Corporation, N.Y., U.S.A.
- (b) n-Decyl mercaptan, supplied by the Columbia Organic Chemicals Co., Columbia, S.C., was distilled and the fraction boiling between 232°C and 235°C was used.
- (c) Thiophene free benzene, supplied by the Merck Co., Montreal, was distilled and the fraction boiling between 77.5°C and 78.5°C was used.
- (d) n-Hexane supplied by the May and Baker Co. (England)

was distilled and the fraction boiling between 65°C and 67°C was used.

Preparation of Coconut Charcoal

The following procedure was used for all samples.

The charcoal was freed from dust by shaking with a 20 mesh sieve. 5 g. samples were accurately weighed and placed in 4 oz. screw cap bottles. To remove oxygen from the charcoal surface, the samples were heated at 300°C for 30 minutes. Nitrogen, from which oxygen was removed by the $\text{CrCl}_2\text{-Zn(Hg)}$ column, was passed over the charcoal during the heating and while cooling. When the bottles were sufficiently cooled for handling, they were sealed with screw caps filled with neoprene rubber washers. After cooling to room temperature, the bottles were evacuated for one hour by means of a hypodermic needle inserted through the seal. This evacuation was carried out in order to aid in the removal of oxygen from the charcoal surface and from the glass of the container. At the end of the evacuation time, the bottles were filled with nitrogen to atmospheric pressure. The filling was accomplished by means of a second hypodermic needle inserted through the neoprene seal. Atmospheric pressure was gauged manometrically.

Preparation of the Mercaptan Solutions

For the initial experiments, 200 mls. of the required concentrations of mercaptan in benzene solution were prepared. The following precautions were taken to avoid oxidation by the atmosphere:

- (a) Individual stocks were made up for each run from freshly distilled benzene.

- (b) Nitrogen was bubbled through the benzene for five minutes to displace any dissolved oxygen before it was added to the mercaptan in volumetric flasks.
- (c) The flasks were securely corked, shaken well and solutions were used on the day of preparation.

For the experiments on the effect of concentration, solvent and temperature, 1 liter stock solutions were prepared. The concentration of these solutions was approximately 0.3M. Benzene and n-hexane were freshly distilled and treated as above.

When these solutions were added to bottles containing prepared charcoal, nitrogen was led in over the charcoal surface. The bottles were quickly sealed after the required volume had been added. The amount of oxygen entering the bottles from the atmosphere was thus kept to a minimum.

Effervescence from the charcoal was noted upon the addition of the mercaptan solutions, furthermore sufficient heat was evolved at this time to noticeably warm the hand. Some of the gas leaving the charcoal was nitrogen. Oxygen, not removed from the charcoal during treatment, would also escape. The heat evolved might be composed of the heats of adsorption of the solvents and the mercaptan and the heat of reaction between oxygen and oxidized carbon products and the mercaptan in the formation of disulphides.

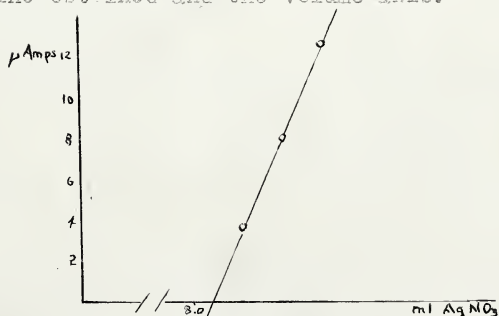
ANALYSIS OF SAMPLES

a) Amperometric Titration

The method of Kolthoff and Harris (21) for the amperometric titration of mercaptans was employed to measure the concentration of

the stock solutions and the equilibrium concentrations of the mercaptan solutions over charcoal. Titration is done in alcoholic solution, the mercaptan being precipitated as silver mercaptide on the addition of AgNO_3 . The end point of titration is found by plotting volume of AgNO_3 added vs. the diffusion current due to excess silver ions.

100 mls. of 95% ethyl alcohol was placed in a 250 ml. beaker, and 3 mls. of 0.1N H_2SO_4 were added as indifferent electrolyte. A pinch of asbestos fibre was added to keep the rotating electrode free from colloidal silver mercaptide (32). The beaker was then placed so that the electrode was immersed and the microburette, containing 0.025N silver nitrate, was swung into place over the beaker. The salt bridge of the cell was then placed in the titration solution and the stirring motor started. A 1 ml. aliquot of the mercaptan solution to be analyzed was added and the AgNO_3 was quickly run in until the first deflection of the microammeter needle occurred. The volume of AgNO_3 and the diffusion current were noted. Several additions of 0.1 mls. of AgNO_3 were made, the current being noted each time. The current delivered was then plotted against the volume of AgNO_3 added to give the end point of titration from the intersection of the straight line obtained and the volume axis:



At the completion of each titration, the platinum electrode and

the salt bridge were rinsed with distilled water, the electrode was wiped dry and the microburette was refilled. Prior to each titration the saturated KNO_3 solution at the salt bridge was changed.

b) Reduction of n-Decyl Disulphide

To measure the amount of oxidation of the mercaptan, the method of I.M. Kiltzoff (22) was employed.

After titration of a sample was completed the mercaptan solution was filtered to free it from charcoal and charcoal dust. 25 mls. of the filtered solutions were placed in a screw cap bottle and 10 gms. of zinc amalgam and 10 mls. of glacial acetic acid were added. The bottle was then sealed and rotated for 45 minutes at room temperature.

A 1 ml. aliquot was then withdrawn, and titrated amperometrically. The concentration of the mercaptan was calculated. The amount of oxidation of the mercaptan was obtained by difference between the concentrations of the reduced solution and that of the unreduced solution.

PROCEDURE AND RESULTS1) The Nature of the Removal of the Mercaptan from Benzene Solution

Previous work (12) had shown that the disappearance of the mercaptan from benzene solution continued until all, or very nearly all, of the mercaptan had been removed. The equilibrium state expected from adsorption was not reached but a decrease in concentration was noted even after 24 hours. These experiments were carried out using glass stoppered erlenmeyer flasks which were not sealed.

If adsorption was responsible for the removal of the mercaptan from solution, an equilibrium state should be reached for any one concentration. The apparent steady increase in the amount of mercaptan removed might be due either to a reaction occurring at the charcoal surface or to oxidation of the mercaptan by air.

To determine the rate of removal of the mercaptan from benzene solution and to measure the extent of oxidation by air, identical samples were prepared. Special precautions were taken to exclude air until each was sealed. These samples were opened at intervals for titration of aliquots. One sample was left sealed for the entire period to serve as a control. From these samples the time required to reach equilibrium and the effect of atmospheric oxidation could be estimated.

50 ml. samples of the freshly prepared mercaptan solution in benzene were added to the charcoal by pipette. A nitrogen atmosphere was maintained in each bottle during the addition of the mercaptan solution. The bottles were then sealed and placed in a constant temperature bath at $25.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ where they were shaken

for six hours.

Analysis of the samples was carried out according to the following schedule:

- (a) One sample was left sealed for the entire six hour period. Then a 1 ml. aliquot was withdrawn for titration.
- (b) Five samples were opened at intervals of 1/2, 1, 1 1/2, 2, 3, 5 and 6 hours for the withdrawal of 1 ml. aliquots. No precautions were taken to exclude air from the bottles while they were open. Screw caps were replaced after each aliquot was withdrawn and the bottles were returned to the constant temperature bath.
- (c) The stock solutions for each run were titrated immediately after the 50 ml. samples were added to the charcoal. This was done so that no error would be introduced due to oxidation of the stock solutions on standing.

It was found that charcoal dust, which resulted from shaking, could be kept out of the pipette used to withdraw aliquots by means of glass tubing partly sealed at one end and packed with glass wool. The tube was of a diameter just wide enough to admit the pipette and long enough to reach half way between the surface of the solution and the charcoal.

The data of this experiment is shown in Tables IA and IB and Figure 1.

TABLE IA

Concentrations of Solutions Used in this Group of Experiments

Sample	Concentration (moles per liter)
13	0.202
14	0.202
15	0.200
16	0.203
17	0.202
18	0.202

TABLE IBGrams of n-Decyl Mercaptan Removed from Benzene Solution per
Gram Coconut Charcoal at $T = 25.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$

Samples						
Time (mins.)	14	15	16	17	18	Average
30	0.045	0.047	0.033	0.035	0.036	0.039
60	0.057	0.055	0.037	0.045	0.053	0.049
90	0.064	0.060	0.052	-	-	0.055
120	0.066	0.064	-	0.051	-	0.062
180	0.070	0.068	0.057	0.061	-	0.080
300	0.090	-	-	0.066	0.097	0.084
360	0.102	0.071	-	0.072	-	0.082

Sample 13 was titrated after six hours when the value obtained for x/m was 0.0571 gm/gm charcoal. This sample was reduced and correcting for the mercaptan converted to disulphide the value for x/m obtained was 0.0331 gm/gm charcoal.

Plots of x/m vs. time for the individual samples showed fairly smooth curves for the first three hours, followed by sudden jumps to higher values of x/m . Comparison of the average final titration value of 0.0844 for samples 14-18, which were opened several times to remove aliquots, with a value of 0.0571 for sample 13 (opened only

once) indicated that atmospheric oxidation was responsible for part of the disappearance of mercaptan from the solutions. The value obtained for sample 13 after reduction is approximately 60% of the value shown by titration of the unreduced sample. This indicated that part of the oxidation was caused by the charcoal itself.

The average values of x/m for these samples are plotted in Figure 1. The points are seen to fall close to a smooth parabolic curve and equilibrium was not reached after six hours.

II) Oxidation of the Mercaptan at the Charcoal Surface

The results of the previous experiments having indicated that oxidation of the mercaptan was occurring as a result of oxygen or other agent on the charcoal surface as well as by oxygen of the air, it was decided to measure the amount of oxidation taking place due only to the material on the surface of the charcoal. To avoid atmospheric oxidation, a sufficient number of samples were prepared so that each bottle need be opened only once.

Stock solutions, approximately 0.2M and 0.1M, were made up and their concentrations were determined amperometrically. 50 mls. of the stock solutions were added to 5 g. samples of the treated coconut charcoal. Five samples of each concentration were made up and individual bottles were opened after shaking in the constant temperature bath at 25°C for 1/2, 1, 2, 3 and 5 hours. 1 ml. aliquots were removed and titrated. Each sample was then reduced and titrated again. The amount of oxidation was obtained from the difference between the two concentrations. This procedure was repeated for each concentration.

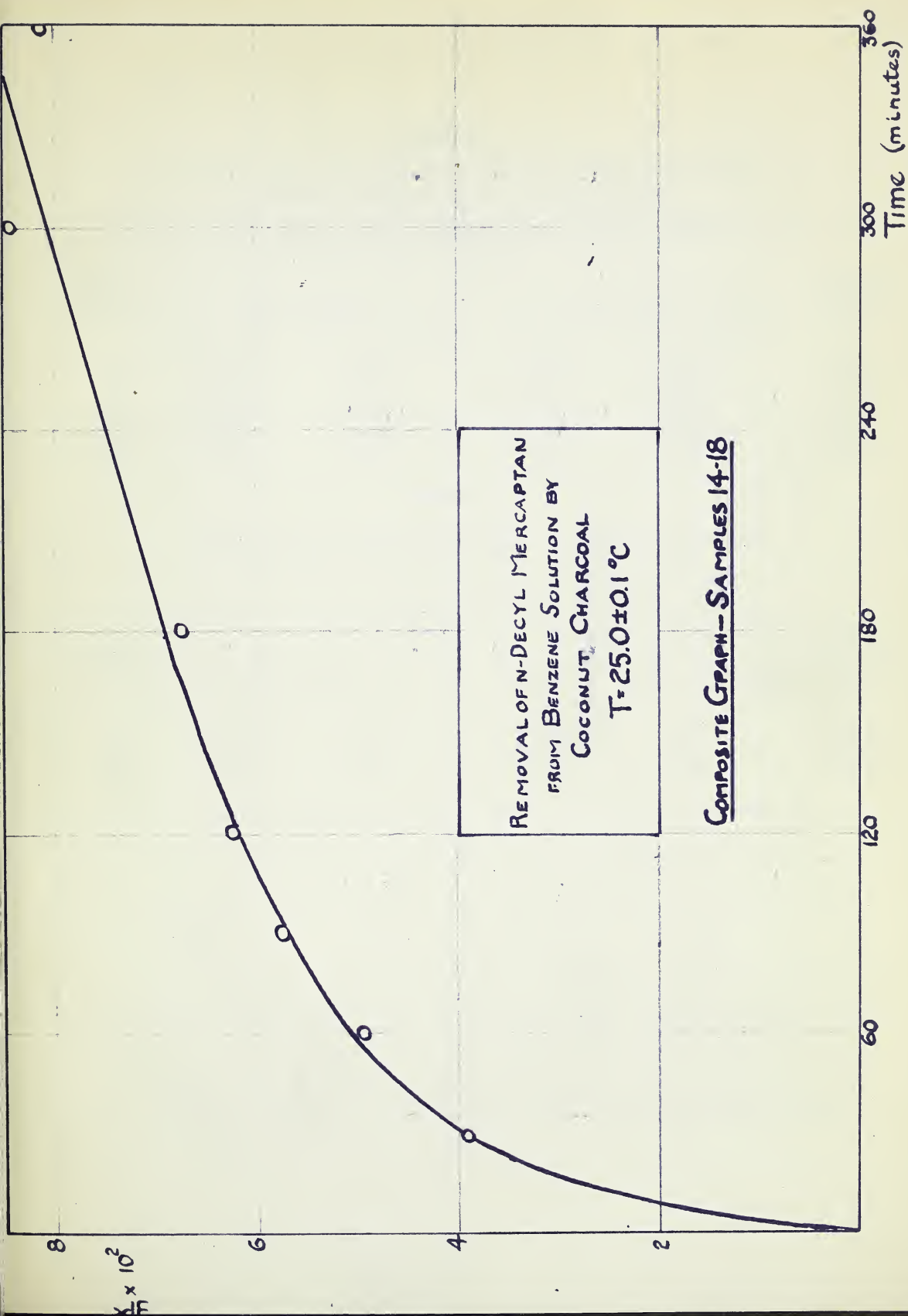


Figure 1

These results are shown in Tables II and IIA and in Figures 2 and 2a.

TABLE II

Grams n-Decyl Mercaptan Removed from Benzene Solution
by Coconut Charcoal at $T = 25.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$

Concentration of Solution 0.1982 M

Time (mins.)	Sample #19		Sample #20		Average Reduced Values
	Titrated	After Reduction	Titrated	After Reduction	
30	0.035	0.028	0.035	0.027	0.027
60	0.042	0.029	0.043	0.029	0.029
120	0.045	0.030	0.046	0.030	0.030
180	0.045	0.032	0.047	0.032	0.032
300	0.046	0.032	0.047	0.033	0.033

TABLE IIA

Grams n-Decyl Mercaptan Removed from Benzene Solution
by Coconut Charcoal at $T = 25.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$.

Concentration of Solution 0.1026 M

Time (mins.)	Sample #21		Sample #22		Average Reduced Values
	Titrated	After Reduction	Titrated	After Reduction	
60	0.031	0.019	0.031	0.019	0.019
180	0.035	0.021	0.035	0.020	0.021
300	0.035	0.022	0.035	0.022	0.022

The following observations may be made from these results:

- (a) The leveling off of the graphs (Fig. 2 and Fig. 2a) of x/m shows that equilibrium was reached, or very nearly so, in about three hours.
- (b) Curve I shows the total amount of mercaptan which has disappeared. Curve II shows the amount of mercaptan which has disappeared by adsorption and is obtained by subtracting the amount of mercaptan converted to disulphide from the total amount which has been removed.

The oxidation to disulphide as measured here was found to decrease slightly at the lower initial concentrations. This is shown by comparing the results shown on Figures 2 and 2a. Starting with 0.1982 M solution, the oxidation amounts to 0.014 gms. mercaptan per gm. charcoal whereas with the 0.1026 M solution, the oxidation was 0.013 gm. per gm. of charcoal.

(c) The rapid initial rise of the graphs shows that the uptake of the mercaptan occurs quickly. Presumably, the available space on the charcoal surface is rapidly covered by solvent and solute molecules.

III) The Effect of Varying Conditions on the Removal of the Mercaptan from Solution.

a) The Effect of Concentration

A decrease in the amount of a substance removed with a decrease in the initial concentration of a solution is a characteristic of adsorption. This effect was noted for the 0.2M and 0.1M solutions of the preceding experiments and should be apparent over a range of concentrations. This change in the amount of mercaptan removed per gram of charcoal might be expected to fit one of the adsorption equations.

A 1 liter stock solution of n-decyl mercaptan 0.3M in benzene was made up. From this, solutions were prepared in concentrations ranging from 0.3M to 0.05M by diluting sufficient volumes of the stock solutions to 200 mls. The concentrations of these solutions were determined after addition of samples to the charcoal. Titration of the stock solution over several days showed that negligible oxidation had taken place.

REMOVAL OF 0.1982 M N-DECYL MERCAPTAN
FROM BENZENE SOLUTION BY
COCONUT CHARCOAL
 $T = 25.0 \pm 0.1^\circ\text{C}$

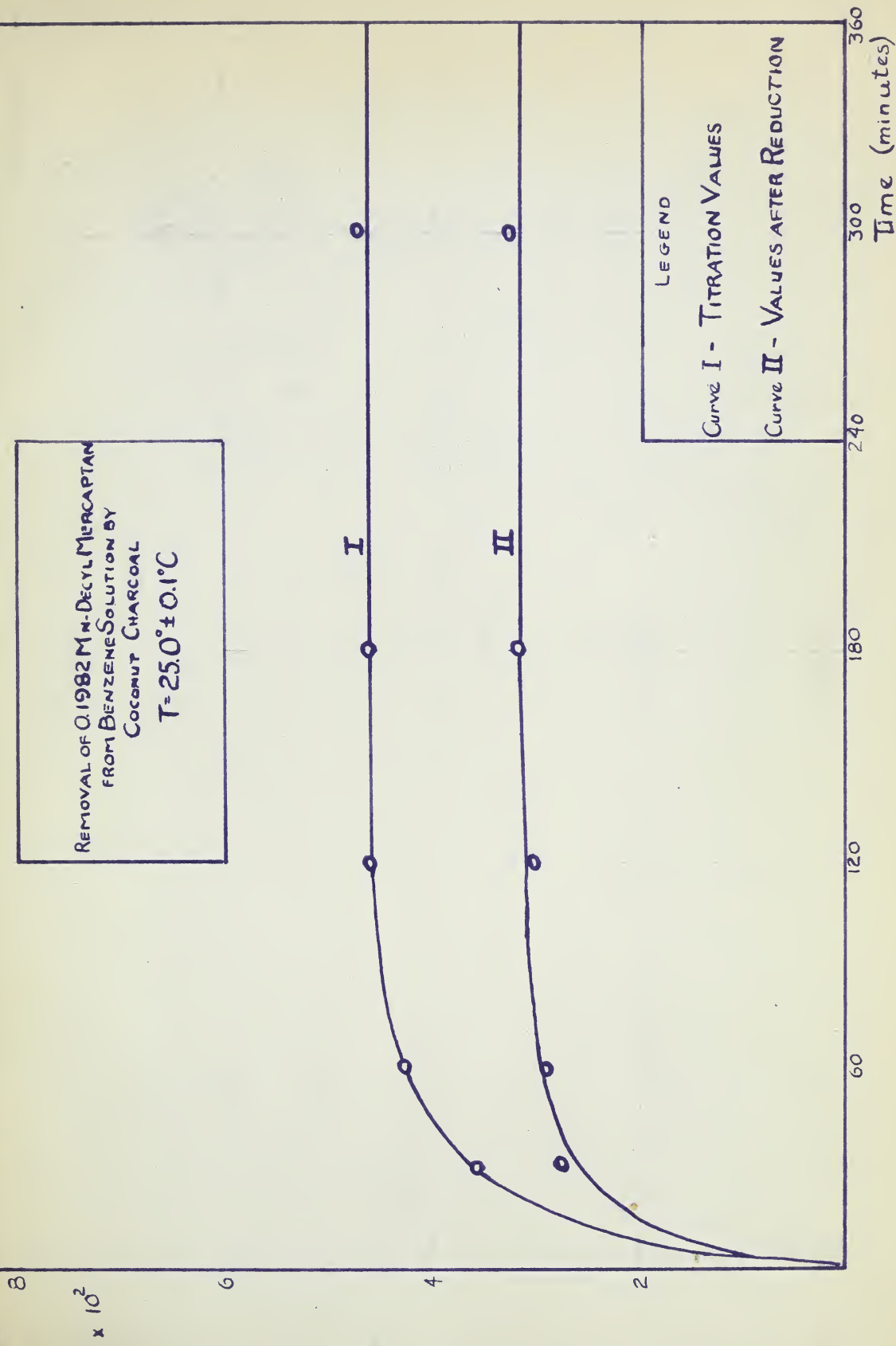


Figure 2

REMOVAL OF 0.1026 M N-DECYL MERCAPTAN
FROM BENZENE SOLUTION BY
COCONUT CHARCOAL
T-25.0°±0.1°C -

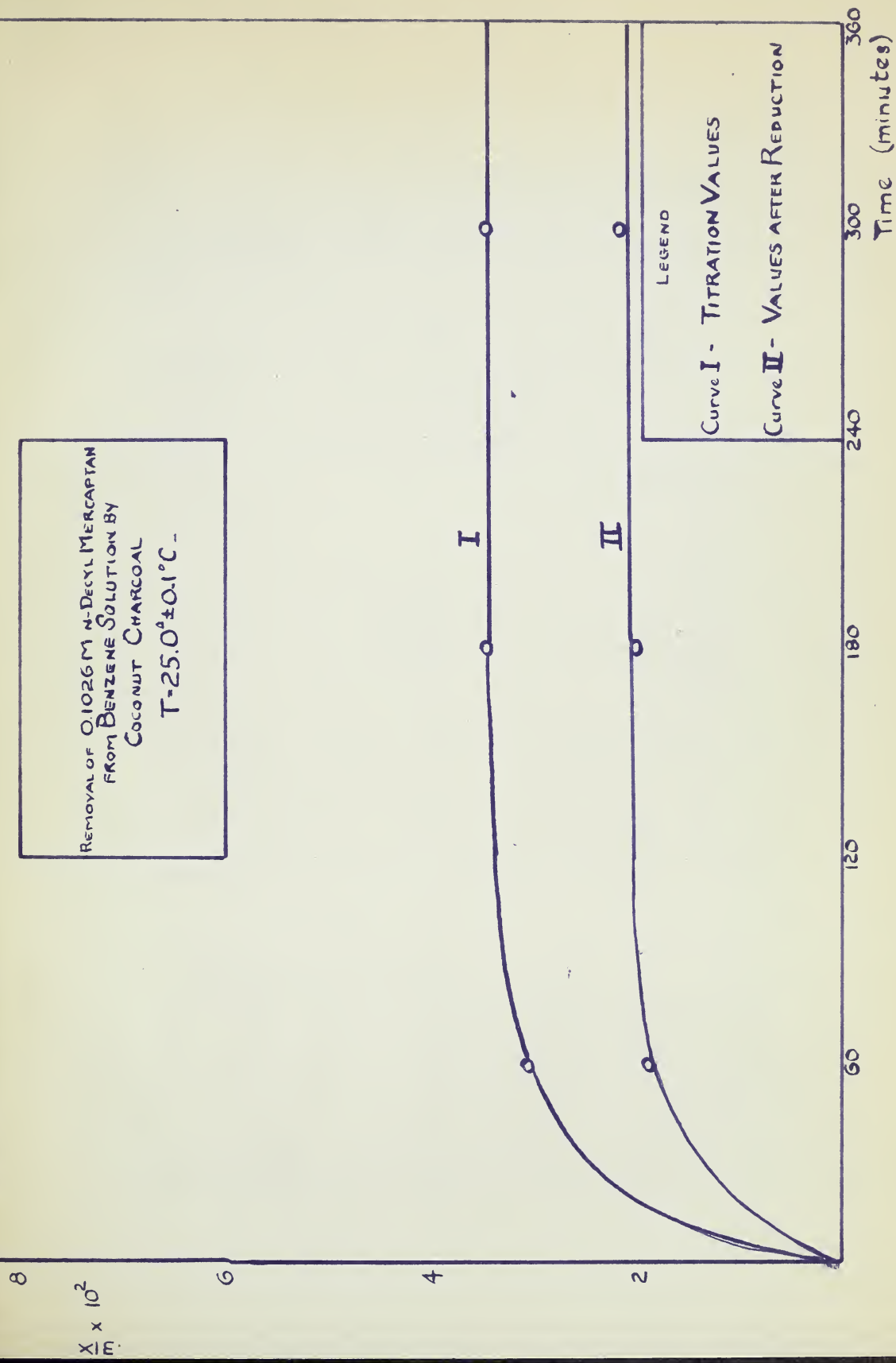


Figure 2d

50 mls. of the various concentrations were added to 5 gms. samples of the charcoal. The samples were shaken in the constant temperature bath at 25°C for five hours. Titration and reduction were carried out as before. The reduced values obtained are shown in Table III. Figure 3 shows a plot of $\log_{10} x/m$ versus $\log_{10} C$.

TABLE III

Removal of n-Decyl Mercaptan from Benzene Solution at
 $T = 25.0^\circ\text{C} \pm 0.1^\circ\text{C}$.

Initial Concentration (moles per liter)	Equilibrium Concentration (moles per liter)	Gms. Mercaptan Removed per gm. Charcoal
C	C_{eq}	x/m
0.305	0.282	0.040
0.207	0.201	0.031
0.198	0.184	0.033
0.131	0.115	0.025
0.103	0.090	0.022
0.077	0.065	0.018
0.054	0.044	0.017

The amount of mercaptan removed per gram of charcoal decreased with the concentrations of the solutions. The plot of $\log_{10} x/m$ versus $\log_{10} C$ gives a straight line from which the following equation was calculated for the Freundlich Isotherm:

$$x = 0.078 p^{0.53}$$

b) The Effect of the Solvent

To determine whether the solvent effected the amount or the rate of removal of the mercaptan from solution, the solvent was changed to n-hexane. It was expected that some difference would be evident because of the unsaturated structure of the benzene ring compared to the saturated structure of hexane. Benzene could be expected

REMOVAL OF N-DECYL MERCAPTAN
FROM BENZENE SOLUTION BY
COCONUT CHARCOAL
 $T = 25.0^{\circ} \pm 0.1^{\circ}\text{C}$
FREUNDLICH ISOTHERM

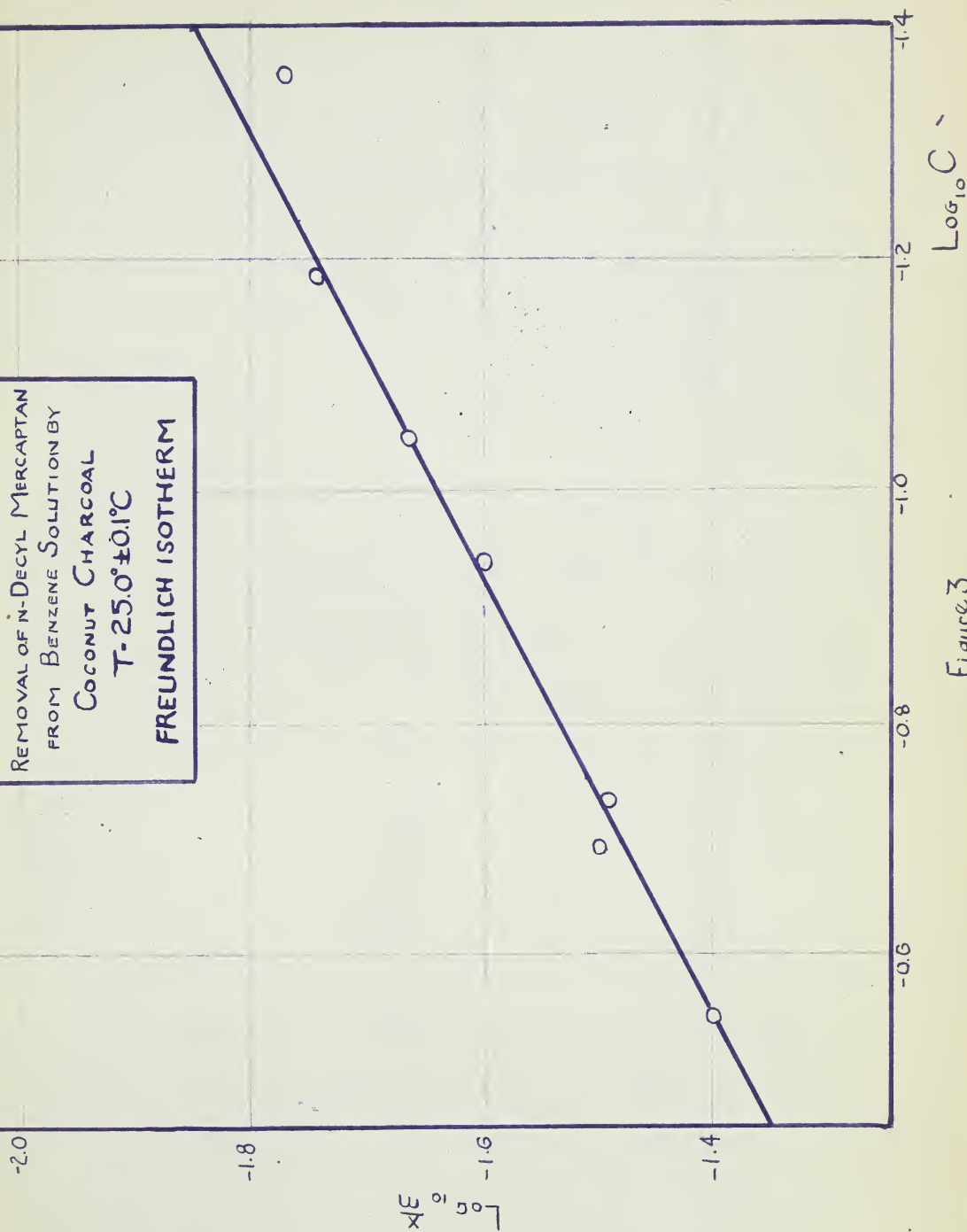


Figure 3

to have a stronger attraction than hexane for the mercaptan and might be more strongly adsorbed than hexane by the charcoal.

A 1 liter stock solution of n-decyl mercaptan approximately 0.3 M in hexane was made up. From this, seven solutions varying in concentration from 0.5M to 0.05M were prepared by diluting sufficient volumes of the stock solution to 200 mls. Concentrations of the stock solutions were determined after addition of samples to the charcoal.

50 mls. of each concentration were added to 5 g. samples of charcoal. These were shaken in the constant temperature bath at 25.0°C for five hours. Titration and reduction were carried out as before. The reduced values of the equilibrium concentrations are shown in Table IV.

TABLE IV

Removal of n-Decyl Mercaptan from n-Hexane Solution at
 $T = 25.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}.$

Initial Concentration (moles per liter)	Equilibrium Concentration (moles per liter)	Gms. Mercaptan Removed per gm. Charcoal.
C	C_{eq}	x/m
0.281	0.217	0.111
0.206	0.152	0.094
0.182	0.139	0.076
0.155	0.107	0.082
0.103	0.065	0.069
0.077	0.043	0.059
0.051	0.025	0.050

Not plotted in Figure 4.

The amount of mercaptan removed per gram of charcoal from the hexane solution was much greater than that removed from the

benzene solution and again decreases with concentration. The values of $\log_{10} x/m$ are plotted against $\log_{10} C$ in Figure 4. A straight line was again produced and yielded the following equation for the Freundlich Isotherm:

$$x/m = 0.193 p^{0.38}$$

These constants differ markedly from those obtained for the removal of the mercaptan from the benzene solution.

c) The Effect of Temperature

In order to determine the effect of an increase in temperature on the amount of removal of the mercaptan and to obtain information for calculation of the heat of adsorption, the temperature of the bath was raised to $35.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$. Smaller values for x/m were expected at the higher temperature.

Five solutions of concentrations varying from 0.25M to 0.05M were made up by diluting sufficient volumes of the stock solution to 200 mls. Concentrations were determined amperometrically.

50 mls. of each solution were added to 5 gm. samples of the charcoal and these were shaken in the constant temperature bath for five hours. Titration and reduction of the samples were carried out as before. The reduced equilibrium concentrations and values for x/m are shown in Table V.

TABLE V

The Removal of n-Decyl Mercaptan from n-Hexane Solution
 $T = 35.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$

Initial Conc. (moles per liter)	Equilibrium Conc. (moles per liter)	Grams Removed per gram of Charcoal x/m
C	C_{eq}	
0.259	0.198	0.106
0.201	0.151	0.089
0.150	0.104	0.079
0.102	0.063	0.068
0.077	0.043	0.059

REMOVAL OF N-DECYL MERCAPTAN
FROM HEXANE SOLUTION BY
COCONUT CHARCOAL
 $T = 25.0 \pm 0.1^\circ\text{C}$
FREUNDLICH ISOTHERM

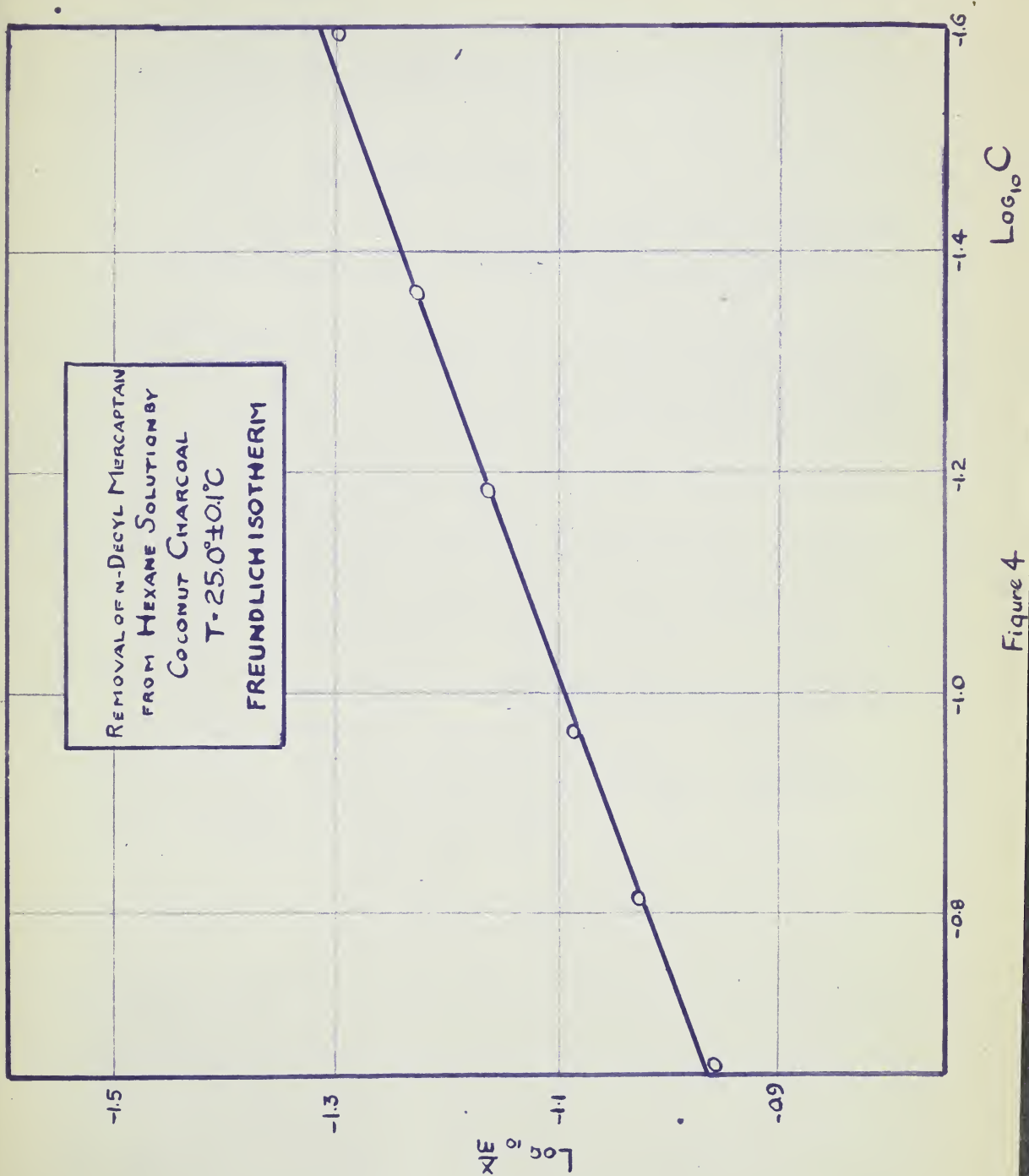


Figure 4

These results are plotted in Figure 5 together with the results from the previous experiments at 25°C in order that the two may be compared.

The amount of mercaptan removed from hexane solution decreased at the higher temperature. The Freundlich Equation calculated from the graph is:

$$x/m = 0.176 p^{0.35}$$

The value for k is quite different from that obtained at the lower temperature. There is little change in the value for $1/n$ however.

Taking x/m as 0.075, calculation by the Clausius Clapeyron equation gives the heat of adsorption from hexane solution as -1.4 k. cal. per mole.

d) Langmuir Isotherms

The results for the removal of n-decyl mercaptan from hexane solution are plotted according to the Langmuir Equation in Figure 6. Straight lines for the graphs of $C/x/m$ vs. C are not found. The lines are concave to the concentration axis instead. The smaller amount of removal of the mercaptan at the higher temperature is evident and the slight difference in x/m for the two temperatures is most noticeable.

REMOVAL OF N-DECYL MERCAPTAN
FROM HEXANE SOLUTION BY
COCONUT CHARCOAL
FREUNDLICH ISOTHERMS

LEGEND
CURVE I (OPEN CIRCLES) $T=25.0 \pm 0.1^\circ\text{C}$
CURVE II (FULL CIRCLES) $T=35.0 \pm 0.1^\circ\text{C}$

$\log_{10} C$

Figure 5

-1.5

-1.3

 $\log_{10} \frac{q}{C}$

-1.1

-0.9

-0.8

-1.0

-1.2

-1.4

-1.6

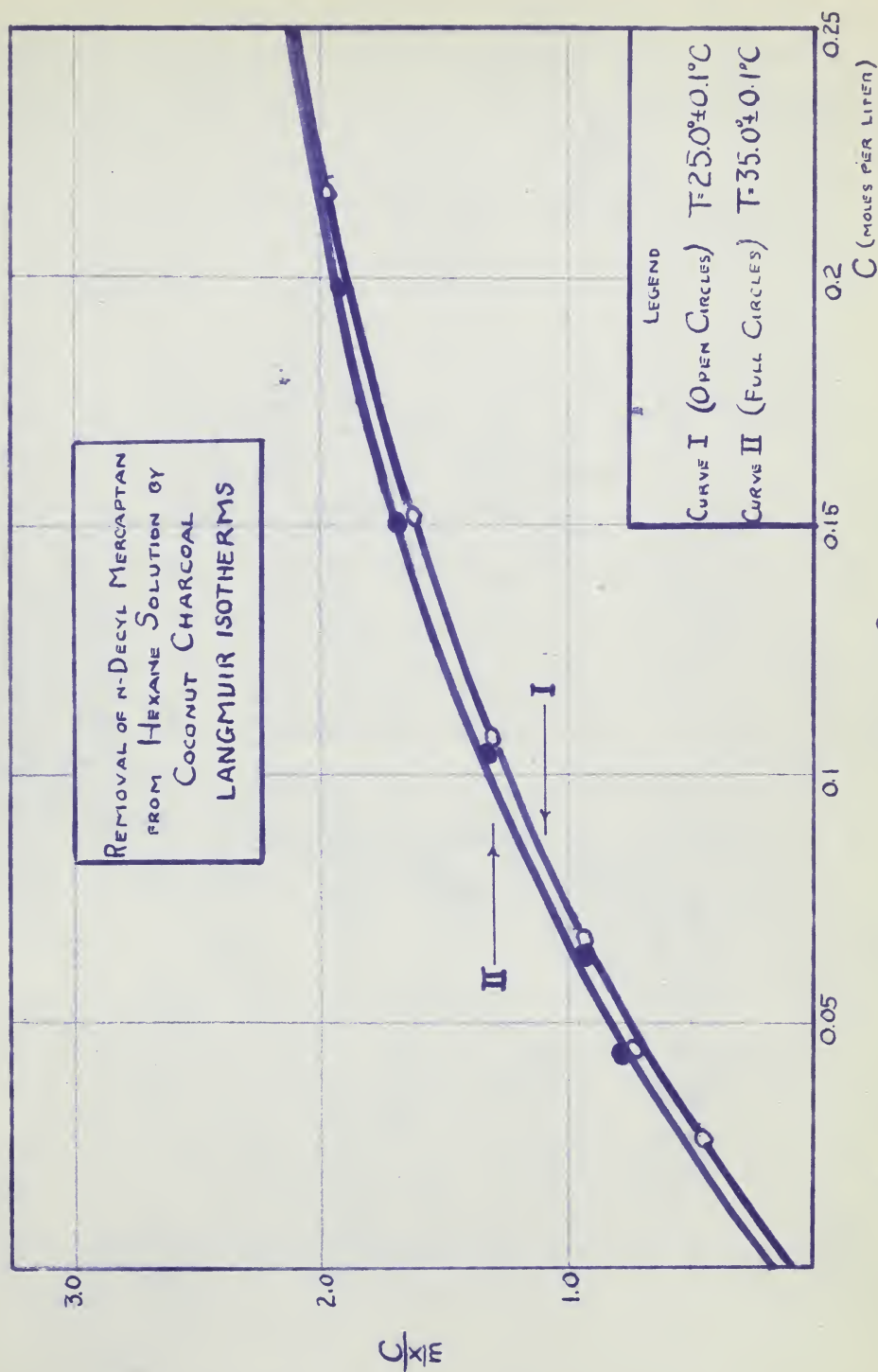


Figure 6

Reliability of Results

The error introduced during the manipulation of the charcoal and the mercaptan solutions is estimated to be less than 5%. This is based upon the assumption that the personal errors introduced in the use of the equipment are constant. The same pipettes, burette and analytical balance were used throughout. A source of error lies in plotting the best fit line in finding the end point of amperometric titrations. However, the scale used in plotting microamperes vs. milliliters of silver nitrate leads to an estimation of the error here as ± 0.03 mls. which is the same as the possible error in the microburette.

DISCUSSION

The extent of removal of n-decyl mercaptan from benzene solution at 25°C by coconut charcoal was quite small, approximately 10% of the initial concentration. With n-hexane as the solvent at this temperature the extent of removal is far greater, varying from 22% for higher concentrations to nearly 50% for lower concentrations. When the temperature was raised by ten degrees the amount of removal from hexane solution was slightly lowered.

The shapes of the graphs of x/m vs. time obtained in Figure 2 and Figure 2a suggest that adsorption is responsible for the removal of the mercaptan from these solutions and the Freundlich Isotherm in Figures 3, 4 and 5 would appear to bear this out. When this same data is plotted according to the Langmuir equation (Fig. 6) the resulting curve shows that adsorption is not monomolecular.

The small value of the heat of adsorption calculated for the hexane solution (-1.4 k. cal. per mole) in no way compares with the results obtained by Ellis and Reid (7) who found that the heat of vaporization for mercaptans increases with molecular weight and is -11.5 k. cal. per mole for nonyl mercaptan. This small value for the heat of adsorption and the fact that the Langmuir equation does not hold, indicates that the mercaptan molecules may be held at the charcoal surface by physical adsorption.

The smaller extent of removal of mercaptan from the benzene solution may be due to association between the benzene and mercaptan molecules. That this attraction could be great enough to retain a majority of the mercaptan molecules in the body of the benzene solution is considered to be possible in the light of the numerous compounds formed by the benzene ring. Such association would not occur with the non-polar hexane solution where the mercaptan molecules would be free to move from the body of the solution to the charcoal surface. A further consideration is that the benzene itself is much more strongly adsorbed than either the mercaptan or hexane. This would result in a practical saturation of the charcoal surface by benzene molecules leaving little space available to the mercaptan.

It is possible that three competing processes occur simultaneously during the process of removal of the mercaptan from hydrocarbon solutions. These are:

- (a) Adsorption and desorption of the solvent molecules.
- (b) Weak adsorption and desorption of the mercaptan molecules.

- (c) Adsorption and desorption of disulphide molecules formed by oxidation of the mercaptan at the charcoal surface.

CONCLUSIONS

1. n-Decyl mercaptan is removed from hydrocarbon solvents to a small extent by coconut charcoal. The adsorption which occurs is physical in character.
2. The amount of removal of mercaptan from benzene solution is less than that removed with hexane as the solvent. This may be due to association between the mercaptan and the benzene. No evidence has been found for this association.
3. Oxidation of the mercaptan to disulphide occurs when coconut charcoal is added. The extent of this oxidation is measurable, the disulphide being reduced by zinc amalgam and acetic acid. The oxidation is increased if the mercaptan solution, over charcoal, is allowed contact with the atmosphere. Charcoal must be present for this oxidation to occur.
4. The amount of mercaptan removed per gram of charcoal increases with increasing concentration. Elevation of the temperature by ten degrees results in slight lowering of the amount of mercaptan removed by charcoal.
5. The heat of adsorption of n-decyl mercaptan from hexane solution is calculated to be -1.4 k. cals. per mole.
6. Over the concentration range 0.3M to 0.05M, the amount of adsorption of n-decyl mercaptan from the two solutions is given by the following equations:

<u>Temperature</u>	<u>Solvent</u>	<u>Freundlich Isotherm</u>
25°C	Benzene	$x/m = 0.078 p^{0.53}$
25°C	Hexane	$x/m = 0.193 p^{0.38}$
35°C	Hexane	$x/m = 0.176 p^{0.35}$

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